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DEODORIZER AND ITS PRODUCTION  
[DASSHUZAI OYOBI SONO SEIZO HOHO]

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[Claim]

[Claim 1]

A deodorizing agent wherein at least one type of element selected from a group made up of an iron element, a copper element, a zinc element, a nickel element and an aluminum element which is carried is a calcium phosphate group compound;

[Claim 2]

A deodorizing agent as described in Claim 1 wherein 1 to 30 wt % of at least one type of element selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element is carried on the abovementioned carrier which is made up of a calcium phosphate group compound;

[Claim 3]

A deodorizing agent as described in Claim 2 wherein 1 to 30 wt % of at least one type selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element is carried respectively on the abovementioned carrier made up of a calcium phosphate group compound;

[Claim 4]

A deodorizing agent as described in Claim 1 wherein the abovementioned calcium phosphate group compound has an appatite structure;

[Claim 5]

A deodorizing agent as described in Claim 4 wherein the mol ratio of the calcium element and the phosphorus element in the abovementioned calcium phosphate group compound is within the range of 1.5 to 1.67 (calcium element/phosphorus element);

[Claim 6]

A deodorizing agent as described in Claim 4 wherein the abovementioned calcium phosphate group compound is hydroxy appatite or halogen appatite;

[Claim 7]

A deodorizing agent as described in Claim 1 wherein three elements-the abovementioned iron element, copper element and aluminum element-are carried;

[Claim 8]

A deodorizing agent as described in Claim 1 wherein at least four elements selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element;

[Claim 9]

A deodorizing agent as described in Claim 8 wherein not more than 20 wt % of the four elements selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element is respectively carrier on the abovementioned carrier made up of a calcium phosphate group compound;

[Claim 10]

A deodorizing agent as described in Claim 8 wherein at least one element selected from a group made up of a titanium element, silver compound and a manganese element is also carried;

[Claim 11]

A deodorizing agent as described in Claim 10 wherein not more than 3 wt % of at least one type of element selected from a group made up of the abovementioned titanium element, silver element and manganese element is carried on the abovementioned carrier made up of a calcium phosphate group compound;

[Claim 12]

A deodorizing agent as described in Claim 8 wherein 1 to 50 wt % of at least four types of element selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element

and at least one type of element selected from a group made up of a titanium element, silver element and manganese element;

[Claim 13]

A method for producing a deodorizing agent wherein at least one type of element selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element is added and dried on a calcium phosphate group compound slurry when making a deodorizing agent on which at least one type of element selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element is carried on a carrier made up of a calcium phosphate group compound;

[Claim 14]

A production method as described in Claim 13 wherein at least one type of metal oxide selected from a group made up of an iron compound, copper compound, zinc compound, nickel compound and aluminum compound is dissolved in the abovementioned calcium phosphate group compound, stirred then dried;

[Claim 15]

A production method as described in Claim 14 wherein the abovementioned metal compound is made into a metal salt;

[Claim 16]

A production method as described in Claim 13 wherein 1 to 30 wt % of at least one type of element selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element is carried on a carrier made up of a calcium phosphate group compound;

[Claim 17]

A production method as described in Claim 16 wherein at least one type of element selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element is carried on the abovementioned carrier which is made up of a calcium phosphate group element;

[Claim 18]

A production method as described in Claim 13 which uses the abovementioned calcium phosphate group compound having an apatite structure;

[Claim 19]

A production method as described in Claim 18 wherein the mol ratio of the calcium element and phosphorus element in the abovementioned calcium phosphate group compound is in the range of 1.5 to 1.67 (calcium element/phosphorus element;

[Claim 20]

A production method as described in Claim 18 wherein the abovementioned calcium phosphorus group compound is hydroxy appatite or halogen appatite;

[Claim 21]

A production method as described in Claim 13 wherein three elements-the abovementioned iron element, copper element and aluminum element-are carried;

[Claim 22]

A production method as described in Claim 13 wherein at least four elements selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element are carried;

[Claim 23]

A production method as described in Claim 22 wherein at most 20 wt % of at least four elements selected from a group made up of the abovementioned iron element, copper



element, zinc element, nickel element and aluminum element is carried on the abovementioned carrier made up of a

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calcium phosphate group compound;

[Claim 24]

A production method as described in Claim 22 wherein at least one element selected from a group made up of a titanium element, silver element and manganese element is carried;

[0025]

A production method as described in Claim 24 wherein not more 3 wt % of at least one element selected from a group made up of the abovementioned titanium element, silver element and manganese element is carried on the abovementioned carrier made up of a calcium phosphate group compound;

[0026]

A production method as described in Claim 22 wherein 1 to 50 wt % of at least four elements selected from a group made up of the abovementioned iron element, copper element, zinc element, nickel element and aluminum element and at least one element selected from a group made up of a titanium element, silver element and manganese element is carried on the abovementioned carrier.

[Detailed Description of Invention]

[0001]

[Industrial Field]

The present invention relates to a deodorizing agent and method for producing same which can remove and reduce foul-smelling constituents and harmful constituents and the like.

[0002]

[Prior Art]

In recent years, as the living environment and lifestyles have become more varied and as the concern for a variety of foul odors (odorants) generated in homes and offices when a variety of products are supplied is heightening, the need to easily remove and reduce foul odors has increased.

[0003]

Foul odors (hereinafter, "odorants") typified by ammonia, trimethyl amine, methyl mercaptan and the like are generally harmful to the environment and may be harmful to

humans. In addition, even odorants which are not harmful can cause discomfort and may induce stress.

[0004]

As a result, foul smelling substances originating in the feces and urine of household pets, foul tobacco odors in offices, bathroom odors, odors in drawers and closets, odors in automobiles and odors in food production plants have traditionally been removed or deodorized. There has been a particularly strong need for removing and reducing these odorants in recent years in order to provide a suitable living environment.

[0005]

A variety of methods have been used to remove and reduce the abovementioned foul odors and other odorants. For example, there is the method which masks odors using an aromatic deodorizer or fragrance and neutralizes the foul odor through a synergistic effect; the method which adsorbs the abovementioned odorants on activated carbon and zeolite and other porous substances and removes them; the method which neutralizes the odorants using an oxidant, reducing agent and the like as well as other methods.

[0006]

However, when a sensory deodorizing method which functions by masking using an aromatic deodorizer or fragrance and the like is used, the odorant itself is still present and there are environmental hygiene problems caused by the odorant. In addition, when the compatibility between the odorant and the aromatic deodorizer and fragrance is poor, there are still problems in that another foul odor is generated.

[0007]

There are also great differences in the adsorbing capability of the activated carbon traditionally used as a deodorizer due to the constituents of the foul odor. There are also limits to the adsorption power (deodorizing power) due to the adsorption effect. In addition, the activated carbon is periodically replaced so that the water portion in the air can prevent foul smelling gas from adsorbing. As a result, it is deficient in that periodic replacement operations are required, the management operations are troublesome and at the same time the long-term costs are high.

[0008]

In addition, when the method which neutralizes the odorants using an acid or an alkali is used, a suitable acid and alkali must be selected to handle the odorant used. The operations and labor involved in making the selection are troublesome and the safety and cost are problematical as well.

[0009]

In keeping with this background, development of a highly safe oxidizing and decomposing catalyst which can be recycled is proceeding apace. Here by "oxidizing and decomposing" is meant reacting the oxygen in the air with ammonia and other odorants and carrying out oxidation and decomposition using iron and aluminum and other metals as a catalyst.

[0010]

Laid-Open Patent Specification 7-171384 discloses impregnating one or more metal acetates on activated carbon and other porous substances; Laid-Open Patent Specification 5-98184 discloses a main agent consisting of zeolite or magnesium silicate and activated alumina and a platinum

metal salt; and Laid-Open Patent Specification 4-66124 discloses carrying a metal oxide made up of zeolite and gold and iron as an oxidation and decomposition catalyst group deodorizer using this type of oxidation decomposition.

[0011]

Nevertheless, the deodorizing power of the oxidation and decomposition catalyst group deodorizing agent based on these technologies was generally insufficient. There were a number of defects which had to be remedied, such as the inferior deodorizing power for methyl mercaptan and other specific gases; the insufficient oxidation and decomposition capability and failure of the deodorizing power to last over long periods of time; and the significant decline in the deodorizing power at ordinary temperature and other low temperature regions.

[0012]

In addition, Patent Publication 62-135411 and Patent Publication 63-147858 disclose a deodorizing agent and activated inorganic material wherein aluminum and iron and

other metal compounds are compounded in hydroxy apatite and tricalcium phosphate and other calcium phosphates. Nevertheless, when this deodorizing agent and inorganic activated material were used, a metal element and a calcium phosphate were simply mixed to make a powder or the powders were only sintered so that the interaction of the metal element and the calcium phosphate on the atomic level was weak. What is more, the dispersion property was low so that the oxidation and decomposition power of the metal element was poor and the deodorizing power was insufficient.

[0013]

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[Problems Which the Present Invention is Intended to Solve]

Taking note of the abovementioned situation of the prior art, it is an object of the present invention to provide a deodorizing agent having an outstanding deodorizing effect on ammonia, trimethyl amine, methyl mercaptan and other odorants, having an effective deodorizing power which lasts for long periods of time, which is highly safe and easy to handle and a method for producing same.

[0014]

[Means Used to Solve the Problems]

The present invention relates to a deodorizer (hereinafter, "deodorizer in the present invention") wherein at least one element selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element is carried on a carrier made up of a calcium phosphate group compound.

[0015]

When the deodorizer in the present invention is used, at least one element selected from a group made up of an iron compound, copper compound, zinc compound, nickel compound and aluminum compound is carried on a carrier made up of a calcium phosphate group compound, thereby providing a deodorizer which efficiently adsorbs ammonia, trimethyl amine and methyl mercaptan and other odorants (foul smelling substances) and further oxidizes and removes these odorants (foul smelling substances) by the catalytic effect of the abovementioned metal elements.

[0016]

This means that a deodorizer is provided which has an outstanding deodorizing effect (deodorization, the same



holds hereinafter) on a variety of odorants, which can prolong the effective deodorizing power over long periods of time, which is highly safe and which is easy to handle.

[0017]

As a result, the deodorizer in the present invention is an oxidation and decomposition catalyst group deodorizer which adsorbs ammonia, trimethyl amine and methyl mercaptan and other odorants on a calcium phosphate group compound and oxidizes and decomposes the abovementioned odorant using the oxidation and decomposition capability of a variety of metal elements which are carried on this calcium phosphate group compound.

[0018]

The present invention relates to a method for producing a deodorizer (hereinafter, "production method in the present invention") wherein at least one element selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element is added to a calcium phosphate group compound when at least one element selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element is used to produce the deodorizer carried

on a carrier made up of a calcium phosphate group compound is added and then dried.

[0019]

When the production method in the present invention is used, a production method for deodorizer can be provided wherein at least one element selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element is added to a slurry of a calcium phosphate group compound and then dried so that the various metal elements indicated above can be carried on the calcium phosphate group compound, having outstanding deodorizing effect on a variety of odorants, can maintain an effective deodorizing power for long periods of time, which is highly safe and which can be handled easily.

[0020]

[Mode of Working the Invention]

When the present invention (hereinafter, the deodorizer in the present invention and the method of production in the present invention are referred to comprehensively as "the present invention") is used, at least one element selected from a group made up of an iron element, copper element, zinc element, nickel element and

aluminum element is carried on a carrier made up of a calcium phosphate group compound; here "carrying" refers to a state of bonding or containing originating in the interaction of the metal elements on the carrier at the atomic level, for example, carrying should be performed by ion exchange and / or adsorbing.

[0021]

In the present invention, an iron element and a variety of other metal elements are carried on a carrier made up of hydroxy appatite and other calcium phosphate group compounds and the ions in the variety of metals are carried by the interaction of the ion exchange with the calcium ions ( $\text{Ca}^{2+}$ ) in the hydroxy appatite (hereinafter, "HAp") or the adsorption on the Hap crystals.

[0022]

In the present invention, 1 to 30 wt % of at least one element selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element should be carried on a carrier made up of a calcium phosphate group compound at total weight of the abovementioned types of metal.

[0023]

We shall describe this in more detail further on, however, when the amount of the various metal elements indicated above carried is less than 1.0 wt %, as indicated above, the catalytic activity for the ammonia, methyl mercaptan and other odorants is insufficient. In addition, when more than 30 wt % is used, the catalytic activity does not increase considering that the amount carried is great and the adsorption of odorants on a carrier made up of a calcium phosphate group compound is hindered.

[0024]

In addition, the lower limit of the amount of the variety of metal elements indicated above which is carried should be 1 wt % while the upper limit should be 20 wt % from the point of view of practicality. In addition, when more than 30 wt % is used, the deodorizing power is obstructed and the performance as a deodorizer deteriorates.

[0025]

As indicated in Figure 3 and Figure 4, the deodorizing power (deodorizing effect) of the aluminum (Al) on ammonia ( $\text{NH}_3$ ) is outstanding. The deodorizing power on the odorants

is oftentimes different depending on the type of metal element used, as indicated by the outstanding deodorizing power (deodorizing effect) of iron (Fe) and copper (Cu) on methyl mercaptan ( $\text{CH}_3\text{SH}$ ).

[0026]

This means that particularly when there are a plurality of odorants present, 1 to 30 wt % of each type of the plurality of metal elements should be carried respectively on the carrier and 1 to 20 wt % of these should be used.

[0027]

In the present invention, a calcium phosphate group compound should be used as the carrier. Examples are: amorphous calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$  : ACP), apatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$  : AP), hydroxy apatite ( $\text{Ca}_{10}(\text{PO}_4)_6$

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$\text{X}_2\text{:Ap}$ ), hydroxyl apatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$  : HAp), fluorine apatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  : FAp), apatite chloride ( $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$  : CAp), octacalcium phosphate ( $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$  : OCP), tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$  : TCP), calcium hydrogenphosphate ( $\text{CaHPO}_4$  : DCP or DCPA, monetite), calcium

dihydrate phosphate ( $\text{CaHPO}_4$ :DCP2 or DCPD, Brushite) and other well-known compounds.

[0028]

These calcium phosphate compounds generally have an adsorbing effect. In particular, the surface area of hydroxy apatite (HAp) is large and has cation sites ( $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{OH}^-$ ) and the surface activity and adsorption action are high.

[0029]

In the present invention, the calcium phosphate group compound should have an apatite structure.

[0030]

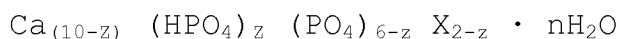
A representative example of the apatite structure is general formula  $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$  ( $\text{X} = \text{OH}, \text{F}, \text{Cl}$  and the like). Usually the mol ratio of the calcium element and the phosphorus element is in the range of 1.5 to 1.67. In addition, apatite has a tunnel structure centering on X ( $\text{X} = \text{OH}, \text{F}, \text{Cl}$  and the like) and transfer of ions and ion replacement is said to readily take place along this tunnel.

[0031]

In the present invention, the calcium phosphate group compound should be hydroxy apatite or halogenated apatite. Of these, hydroxy apatite is particularly suitable. HAp is expressed by the chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$  and it has a basic composition wherein the mol ratio of the calcium element and the phosphorus element is 1.67 (calcium element /phosphorus element = 1.67). However, the ratio of the calcium element and the phosphorus element (calcium element / phosphorus element) sometimes fluctuates due to the type of metal element carried and the amount carried and the crystallinity sometimes fluctuates as well. In the present invention, a substance may be used wherein the crystallinity fluctuates and which may be amorphous as well. Furthermore, halogenated apatite (fluorine apatite:  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ), apatite chloride:  $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ ) and the like which have been substituted by fluorine and chlorine and other halogen elements instead of the OH group in the abovementioned  $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$  may be used.

[0032]

This means that in the present invention, the substance expressed by the following chemical formula is a suitable carrier.



(however,  $Z = 0$  to  $1$ ,  $n = 0$  to  $1$ ,  $X =$  an OH group or a halogen element).

[0033]

In the present invention, three types of elements, particularly, an iron element, copper element and an aluminum element may be carried on a carrier made up of a calcium phosphate group compound

[0034]

As indicated above, as is the case with aluminum which has outstanding deodorizing power (deodorizing effect) on ammonia ( $\text{NH}_3$ ) and iron (Fe) and copper (Cu) which have an outstanding deodorizing power (deodorizing effect) on methyl mercaptan ( $\text{CH}_3\text{SH}$ ), the deodorizing effect on an odorant oftentimes differs depending on the type of metal element. This means that particularly if an iron element, copper element and aluminum element are carried, a deodorizing agent which has an excellent deodorizing power on ammonia ( $\text{NH}_3$ ) and methyl mercaptan ( $\text{CH}_3\text{SH}$ ) and the like can be obtained even when a deodorizing agent having this structure is used. Depending on the type used, the amount carried should be 1 to 30 wt % relative to the carrier and the wt % should be within the range of 1 to 30 wt %.



[0035]

In addition, at least four types of elements selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element can be carried in the present invention.

[0036]

In this case, not more than 20 wt % of at least four types of elements selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element respectively can be carried on a carrier made up of a calcium phosphate group compound.

[0037]

We shall describe this in greater detail later on. However, in particular, 6 to 12 wt % of an iron element, copper element and zinc element and 1 to 6 wt % of a nickel element and aluminum element respectively should be carried.

[0038]

In particular, at least four types of elements selected from a group made up of the abovementioned iron

element, copper element, zinc element, nickel element and aluminum element can be carried for a deodorizing agent carried on a carrier made up of a calcium phosphate group compound and at least one type of element selected from a group made up of a titanium element, silver element and manganese element can be carried.

[0039]

In this case, not more than 3 wt % of at least one type of element selected from a group made up of a titanium element, silver element and manganese element can be carried on a carrier made up of a calcium phosphate group compound.

[0040]

Furthermore, when at least four types of elements selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element and at least one type of element selected from a group made up of a titanium element, silver element and manganese element are carried on a carrier made up of a calcium phosphate group compound, the total amount of each of these metal elements carried should be in the range of 1 to 50 wt %.

[0041]

When the total amount of the wt % of each of the abovementioned metal elements is carried, its catalytic activity as an oxidation and decomposition catalyst is insufficient. In addition, when the total amount carried exceeds 50 wt %, the catalytic activity declines even though the amount carried is great and the absorption of the odorant on the calcium phosphate group compound is hindered.

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[0042]

In addition, in the present invention, the shape can be made to fine particles to increase its effect as a deodorizing agent and the mean particle size of the fine particles can be in the range of 1 to 70  $\mu\text{m}$ . However, it should by no means be construed that the formulation of the deodorizing agent in the present invention is restricted to these.

[0043]

When the substance is made into powdered fine particles having a mean particle size of 1 to 70  $\mu\text{m}$ , the surface area of the deodorizing agent is increased and the

amount of adsorption of the ammonia, trimethyl amine, methyl mercaptan and other odorants increases and the amount of decomposition of these odorants should be increased. Those having a small mean particle size are such that the surface area of the deodorizing agent should be large, however, when it is too small, aggregation and the like occur and the deodorizing power deteriorates.

[0044]

The form in which the deodorizing agent in the present invention is used may be as is as a mixture powder having the abovementioned structure. However, this mixed powder may also be used in the form of a slurry type coating. The binder used at this time may be aluminum hydroxide, glass powder, water glass, colloidal silica and the like.

[0045]

In addition, the abovementioned mixed powder has a small mean particle size so that when it is dispersed in the abovementioned slurry and the like, a dispersed medium should be used. This dispersed medium may be a substance such as water, alcohol and other organic solvent which evaporates in the process whereby a coated film is formed after the abovementioned coating is coated and dried or

baked. In addition, when the mixed powder in the coating aggregates, an additive may be added as appropriate to stabilize the dispersion.

[0046]

Furthermore, metal, ceramic, glass and a variety of other types of material may be used as a base material which uses the deodorizing agent in the present invention as a coating.

[0047]

In addition, the deodorizing agent in the present invention may be used as a coating for the inside walls of refrigerators, cooking appliances and the like, air passages for air conditioners, heaters and the like and heating element surfaces, the surfaces of walls which are close to heating elements and the interiors of rooms and the like. It can also be formed on a honeycomb-shaped base material, it can itself be formed to a honeycomb shape and used by installing at locations where the atmosphere (in particular the air) which contains the odorant (foul-smelling gas) flows.

[0048]

In addition, besides mixing the deodorizing agent in the present invention in a coating material as indicated above, it can be mixed beforehand with a raw material which is suitable for the base material and a deodorizing power can be provided to a film, sheet, furniture part, building material and the like having a deodorizing action. The base material used here may be polyethylene, polypropylene, polyamide, polyvinyl chloride, polyethylene and other synthetic resins, as well as vegetable fiber or inorganic substance fiber (paper, cloth, non-woven cloth, leather and the like) as well as molded products made of a variety of natural wood materials and plastics and the like which are used for construction materials.

[0049]

Thus, the molded products containing the deodorizing agent in the present invention may be installed inside coops for livestock, pets and the like and floors and the like. They may also be used for cat litter, toilet paper and the like. As a result, foul odors from livestock and pets as well as unpleasant odors from substances which are themselves the source of foul odors can be removed and reduced efficiently.

[0050]

In the method for producing the present invention, at least one type of metal compound selected from a group made up of an iron compound, copper compound, zinc compound, nickel compound and aluminum compound can be dissolved or suspended. After it has been stirred sufficiently, it is dried and can be molded into a deodorizing agent. In addition, after drying it may be sintered (baked). Also, after it has been dried or sintered, it is pulverized using a sieve having a suitable coarseness and made into powdered fine particles. In addition, each of the abovementioned metal compounds may be a nitrate and other metal salt.

[0051]

In addition, there are no particular restrictions on the method used to carry each of the abovementioned metal elements on a carrier made up of a calcium phosphate group compound. Besides the well-known method involving making a slurry of a carrier made up of hydroxy apatite and other calcium phosphate group compound and mixing and processing a compound containing this slurry and a variety of metal elements, the metal element can be carried on hydroxy apatite and other calcium phosphate group compounds even

using a well-known method which involves mixing and processing the compound containing each of the metal elements while the calcium phosphate group compound is prepared or after it is prepared.

[0052]

In the present invention, there are no particular restrictions on the method used to prepare the calcium phosphate group compound and the dry solid phase reaction method, the wet precipitation reaction method, the wet hydrolysis method, the hydrothermal hydrolysis method and other well-known synthesizing method may all be used. In addition, the mol ratio of the calcium element and the phosphorus element may be varied as appropriate when the calcium phosphate group compound is prepared.

[0053]

[Practical Examples]

Next, we shall describe the present invention using specific examples of it. However, it should by no means be construed that the present invention is restricted to these practical examples.



[0054]

Practical Examples 1 to 49

First, we shall describe practical examples wherein one, two or three types of elements are selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element for the calcium phosphate group compound as well as the comparative examples indicated below.

[0055]

The method for synthesizing the hydroxy apatite involves suspending 135 g of hydroxy apatite (mol ratio of calcium element and phosphorus element: calcium element/phosphorus element = 1.67) which was synthesized using the solution phase method used in the prior art in distilled water and making a slurry out of it. In addition, we weighed out an appropriate amount of the metal element in keeping with the type and carrying amount described in Table 1 as follows in the form of a metal salt and dissolved it in 500 mL of distilled water.

[0056]

We added an aqueous solution of the abovementioned slurry and the metal salts and stirred it for 24 hours at

room temperature. Then, we washed the precipitate thoroughly using distilled water and dried the precipitate for 48 hours at 120°C. After it had dried, we pulverized it using a 200 mesh and obtained the deodorizing agent.

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[0057]

However, it should be kept in mind that the abovementioned metal salts used nitrates of the following: Fe (NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O as the iron salt; Cu (NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O as the copper salt; Zn (NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O as the zinc salt; Ni (NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O as the nickel salt; and Al (NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O as the aluminum salt. In addition, the Fe, Cu, Zn, Ni and Al in the following Table 1 indicate the metal ions for the aqueous solution of the nitrate mixed with the slurry carrier. The values in the table indicate the amount of the metal ions or element carried (wt %) on the hydroxy apatite (HAp) carrier.

[0058]

#### Comparative Example 1

This is a deodorizing agent made up solely of activated carbon.

[0059]

Comparative Example 2

This is a deodorizing agent which did not carry any metals and is made up solely of hydroxy appatite (HAp).

[0060]

Comparative Example 3

This is a deodorizing agent which does not carry any metals and is made up solely of tricalcium phosphate (TCP).

[0061]

Comparative Example 4

This is a deodorizing agent which does not carry any metals and which is made up solely of calcium hydrogenphosphate (Brushite).

[0062]

Comparative Example 5

This is a deodorizing agent wherein an iron oxide ( $\text{Fe}_3\text{O}_4$ ) is compounded in hydroxy appatite. However, it should be noted that the powder-form hydroxy appatite and the powder-form iron oxide are mixed and are then sintered. As indicated in this practical example, no metal is carried on the hydroxy appatite. In addition, the values indicated

in the table indicate the mixed amount (wt %) of the iron element relative to the hydroxy appatite).

[0063]

#### Comparative Example 6

This is a deodorizing agent wherein aluminum nitrate ( $\text{Al}(\text{NO}_3)_3$ ) is compounded in hydroxy appatite. However, it should be noted that the powder-form hydroxy appatite and the powder-form aluminum nitrate are mixed. As indicated in this practical example, no metal is carried on the hydroxy appatite. In addition, the values in the table indicate the amount (wt %) of the aluminum element compounded relative to the hydroxy appatite.

[0064]

#### Deodorizing Effect Test

We measured the amount of both ammonia ( $\text{NH}_3$ ) and methyl mercaptan ( $\text{CH}_3\text{SH}$ ) odorants (foul-smelling substances) deodorized by the deodorizing agent in Practical Examples 1 through 49 and in Comparative Examples 1 through 6 using the following test method. Results are indicated in Table 1.

[0065]

#### 1. Ammonia Deodorizing Test

We injected 30 mL of aqueous ammonia at a concentration of 29 wt % in a 100 mL capacity vial and sealed it using an aluminum seal. We removed the ammonia gas generated inside the container using an injection device and used it for the ammonia deodorizing test.

[0066]

We weighed out 0.5 of the deodorizing agent for each of Practical Examples 1 through 49 and Comparative Examples 1 through 6, placed these respectively in a 1 L capacity "tetrapak" and then fed air to it. Next, we injected ammonia gas in the tetrapak containing the deodorizing agent and kept it for 30 minutes at the prescribed temperature. Then, we measured the concentration of the residue using a gas detection tube (ammonia detection tube manufactured by Gastek Ltd., methyl mercaptan detection tube made by Gastek Ltd.; the same holds hereinafter).

[0067]

We again injected the same amount of the aqueous ammonia into the tetrapak and kept it for 30 minutes at the prescribed temperature and then measured the concentration

of the residue. We repeated these operations 10 times and computed the amount deodorized based on the concentration of the residual odor (concentration of residue) at this time.

[0068]

There were two temperature conditions: room temperature (approximately 23°C) and 60°C. Furthermore, the concentration of the ammonia gas added per time is 2000 ppm. The amount of ammonia deodorized (mg) per 1 g of the sample was computed based on the following formula (1).

[0069]

Amount deodorized (mg/g) = [(total concentration added (ppm) - residual odor concentration (ppm)) divided by  $10^6$ ] x (1/22.4) x 17 x  $10^3$  (mg)] /sample wt (g)  
...formula (1)

[0070]

## 2. Methyl Mercaptan Deodorizing Test

We used 0.1 wt % concentration methyl mercaptan standard solution and used it for the methyl mercaptan deodorizing test.

[0071]

We weighed out 0.1 g of the deodorizing agent produced as indicated above for each of Practical Examples 1 through 49 and Comparative Examples 1 to 6. We placed these respectively in a 1 L capacity tetrapak and blew in air. Next, we injected methyl mercaptan gas in the tetrapak containing the deodorizing agent and kept it for 30 minutes at the prescribed temperature. Then, we measured the concentration of the residue using the gas detection tube.

[0072]

We again injected the same amount of the methyl mercaptan gas in the tetrapak and kept it for 15 minutes at the prescribed temperature and then measured the concentration of the residue. We repeated these operations five times and computed the amount deodorized based on the concentration of the residual odor (concentration of residue) at that time.

[0073]

There were two temperature conditions, room temperature (approximately 23°C) and 60°C. Furthermore, the concentration of the methyl mercaptan added per time was 130 ppm. In addition, the amount of methyl mercaptan

deodorized per 1 g of the sample was computed using the following formula (1).

[0074]

Amount deodorized (mg/g)=[{(total concentration added  
(ppm)- concentration of residual odor (ppm))/  
 $10^6$  } x (1/22.4) x 48 x  $10^3$  (mg)] /sample wt (g)  
.. formula (2)

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[0075]

Results of the deodorizing test for the abovementioned catalytic composition are indicated in Figure 1 through Figure 6 in Table 1 as follows.

[0076]

However, it should be noted that the practical example indicated in Figure 5 and Figure 6 is Practical Example 41. The comparative example is Comparative Example 1. Figure 5 indicates measurement of the deodorizing results on ammonia. It indicates the changes in the concentration of the residual odor when 2000 ppm of ammonia gas is added each time every 30 minutes. Figure 6 indicates measurement of the deodorizing effect on the methyl mercaptan and



indicates the changes in the concentration of the residual odor when 130 ppm of methyl mercaptan is added per time. Those having a small residual odor concentration have a high deodorizing power.

[0077]

Table 1A (Catalyst Composition and Deodorizing Results

Practical Example	Catalyst		
	Composition (HAp + metal element)		Deodorizing Effect
	(amount adsorbed)		(mg/g)
	Amount of metal	N group malodorous	S group malodorous
	added (wt %)	gas: NH <sub>3</sub>	gas: CH <sub>3</sub> SH
		Room Temperature	Room Temperature
	Fe, Cu, Zn, Ni, Al	60°C	60°

1	1	—	—	—	—	2.45	3.63	0.22	0.33
2	—	1	—	—	—	1.52	2.16	0.25	0.4
3	—	—	1	—	—	1.63	2.53	0.23	0.37
4	—	—	—	1	—	1.48	2.09	0.19	0.29
5	—	—	—	—	1	2.45	3.89	0.15	0.22
6	3	—	—	—	—	4.9	7.15	0.33	0.53
7	—	3	—	—	—	2.89	4.34	0.4	0.61
8	—	—	3	—	—	3.42	5.1	0.39	0.6
9	—	—	—	3	—	2.81	3.91	0.3	0.45
10	—	—	—	—	3	5.02	7.63	0.26	0.38
11	10	—	—	—	—	6.12	9.06	0.66	0.92
12	—	10	—	—	—	5.43	8.31	0.63	0.89
13	—	—	10	—	—	4.8	6.67	0.54	0.86
14	—	—	—	10	—	4.55	6.6	0.47	0.69
15	—	—	—	—	10	15.85	23.62	0.28	0.42
16	30	—	—	—	—	7.34	10.87	0.82	1.19
17	—	30	—	—	—	7.06	9.56	0.82	1.07
18	—	—	30	—	—	6.01	10.8	0.7	1.11

[0078]

Table 1 B (Catalyst Composition and Deodorizing Results)

Practical Example	Deodorizing		
	Catalyst Composition		Results (amount
	(HAp + metal element)		adsorbed)
			(mg/g)
	Amount of metal added	N group malodorous	S group malodorous
	(wt %)	gas: NH <sub>3</sub>	gas: CH <sub>3</sub> SH
		Room temperature	Room Temperature
	Fe, Cu, Zn, Ni, Al	60°C	60°C

19	—	—	—	30	—	5.9	8.67	0.54	0.86
20	—	—	—	—	30	19.02	28.34	0.33	0.55
21	0.5	0.5	—	—	—	2.85	4.13	0.29	0.38
22	1	1	—	—	—	3.42	5.06	0.35	0.53
23	1	—	1	—	—	3.21	4.88	0.33	0.49
24	1	—	—	1	—	3.05	4.55	0.29	0.33
25	1.5	—	—	—	0.5	4.93	7.48	0.21	0.31
26	3	3	—	—	—	6.53	9.4	0.7	1.05
27	3	—	3	—	—	5.01	7.41	0.51	0.78
28	3	—	—	3	—	3.85	5.74	0.35	0.52
29	3	—	—	—	3	7.52	11.28	0.58	0.85
30	—	1	2	—	—	2.95	4.41	0.32	0.47
31	—	1	—	2	—	3.05	4.61	0.31	0.48
32	—	2	—	—	1	4.82	7.05	0.25	0.37
33	1	—	—	—	9	8.85	13.27	0.22	0.29
34	5	—	—	—	5	7.29	11.8	0.57	0.79
35	9	—	—	—	1	4.43	6.65	0.7	0.91
36	0.2	0.4	0.4	—	—	2.91	4.36	0.3	0.41

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[0079]

Table 1C (Catalyst Composition and Deodorizing Results)

Practical Example	Deodorizing								
	Catalyst Composition					Results (amount			
	(HAp + metal element)					adsorbed)		(mg/g)	
	Amount of metal added					N group malodorous		S group malodorous	
	(wt %)					gas: NH <sub>3</sub>		gas: CH <sub>3</sub> SH	
						Room temperature		Room Temperature	
	Fe, Cu, Zn, Ni, Al					60°C		60°C	

37	1	1	1	—	—	5.23	7.33	0.53	0.79
38	—	1	1	1	—	5.51	8.82	0.61	0.92
39	—	—	1	1.5	0.5	6.35	8.89	0.74	1.04
40	2	3	4	—	—	7.32	10.76	0.8	1.28
41	6	6	—	—	6	9.25	13.87	0.91	1.18
42	10	10	10	—	—	8.79	13.11	0.96	1.34
43	12	12	—	—	12	17.45	23.78	4.71	6.12
44	8	8	—	—	8	11.38	15.93	2.53	3.39
45	20	—	—	—	—	6.88	9.63	0.75	1.05
46	—	20	—	—	—	6.09	8.83	0.75	1.15
47	—	—	20	—	—	5.74	8.24	0.7	1.01
48	—	—	—	20	—	5.45	7.66	0.54	0.91
49	—	—	—	—	20	17.75	24.85	0.35	0.56

[0080]

Table ID (Catalyst Composition and Deodorizing Results

Practical Example	Deodorizing								
	Catalyst Composition					Results (amount			
	(HAp + metal element)					adsorbed)		(mg/g)	
	Amount of metal added					N group malodorous		S group malodorous	
	(wt %)					gas: NH <sub>3</sub>		gas: CH <sub>3</sub> SH	
						Room temperature		Room Temperature	
	Fe, Cu, Zn, Ni, Al					60°C		60°C	
1	—	—	—	—	—	1.06	0.61	0.161	0.06
2	—	—	—	—	—	1.06	0.85	0.118	0.096
3	—	—	—	—	—	<0.61	<0.3	0.096	0.085
4	—	—	—	—	—	<0.30	<0.3	0.118	0.095
5	10	—	—	—	—	2.04	2.88	0.22	0.28
6	—	—	—	—	10	5.01	7.13	0.172	0.22

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[0081]

Based on the < Results> in Table 1, the deodorizing agent in the present invention has an outstanding deodorizing effect even on ammonia, methyl mercaptan and

other odorants and it was found that the temperature rose as did the deodorizing performance.

[0082]

It was also found that the deodorizing effect of the deodorizing agents in this practical example for at least one of these odorants was equal to or greater than activated carbon (Comparative Example 1).

[0083]

In addition, as can be seen from Figure 3 and Figure 4 (Practical Examples 1 through 20 and Practical Examples 45 through 49 and Comparative Example 2), aluminum (Al) has an outstanding deodorizing power (deodorizing effect) on ammonia ( $\text{NH}_3$ ). It was found that just as iron (Fe) and copper (Cu) have an outstanding deodorizing power (deodorizing effect) on methyl mercaptan ( $\text{CH}_3\text{SH}$ ), the deodorizing power is different on odorants depending on the type of metal element or ions.

[0084]

Therefore, it can be seen that particularly when a plurality of odorants are present, a plurality of types of metal elements can be carried. In addition, as the amount

of one type of carried metal constituent increases, the amount of odorant adsorbed does not increase. When too little is carried, the amount adsorbed declines so that 1 to 30 wt % of one type can be carried on a carrier. In addition, carrying 1 to 20 wt % is preferable.

[0085]

In addition, as can be seen from Figure 1 and Figure 2, the amount of deodorization of either an ammonia or a methyl mercaptan odorant oftentimes declined when one type of carrier metal constituent is used. However, it can be seen that two or more types of carrier metal constituents (Practical Examples 22 through 44) oftentimes have an increased deodorizing power on both the ammonia and methyl mercaptan odorants by adding two or more types.

[0086]

In particular, the deodorizing agents (Practical Examples 41, 43, 44) which carry three types of metal elements, iron, copper and aluminum, have an outstanding deodorizing effect on both ammonia and methyl mercaptan odorants.

[0087]

It can also be seen from Practical Examples 36, 37 and 42 and Practical Examples 41, 23 and 44 that even when a plurality of types of carrier metal constituent are used, as is the case when one type of carrier is used, as the total amount carried increases, the amount of odorant adsorbed (deodorizing power) increases. However, it should be noted that in Practical Example 44, the total amount carried is somewhat greater than 36 wt % so that there is somewhat of a decline in the deodorizing power.

[0088]

As a result, as indicated in Figure 1 and Figure 2, when the total amount of each of the abovementioned metal elements carried is less than 1.0 wt %, the catalytic activity on the ammonia and methyl mercaptan and other odorants is insufficient. It was also found that when the total amount carried exceeded 30 wt %, the catalytic activity was not improved despite the fact that a great deal was carried and the adsorption of the odorant on a carrier made up of a calcium phosphate compound was impeded.



[0089]

Therefore it was found that 1 to 30 wt % of at least one type of element selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element should be carried on a carrier made up of a calcium phosphate group compound at the total weight of each of the abovementioned metals.

[0090]

In addition, the lower limit of the amount of each of the abovementioned types of metal elements carried should be 1 wt % and the upper limit should be 20 wt % for practical considerations. In addition, when more than 30 wt % is used, the deodorizing power is hindered and the performance as a deodorizing agent deteriorates.

[0091]

In addition, as can be seen in Comparative Examples 1 through 4, the temperature rises and at the same time, the adsorbed odorant is removed once so that the odorant is not readily adsorbed in the activated carbon (Comparative Example 1) and the calcium phosphate group compound (Comparative Examples 2 through 4) using only a physical adsorption of the odorant.

[0092]

In addition, as indicated in Figure 5 and Figure 6, in a comparative example (here, Comparative Example 1), the amount of the odorant adsorbed is saturated so that each time the procedure is repeated, the deodorizing power declines conspicuously. On the other hand, when the deodorizing agent in this practical example is used (in Figure 5 and Figure 6, this refers to the deodorizing agent in Practical Example 41), a considerably greater amount of odorant than in the comparative examples is deodorized. As a result, it was found that the deodorizing agent in this practical example adsorbed sufficiently continuously without the odorant being gradually released through repeated use. Thus, in this practical embodiment of the present invention, it is believed that decomposition (oxidation decomposition) of the odorant occurs efficiently through the catalyst action of the adsorbed metal.

[0093]

In addition, in Comparative Examples 5 and 6, the metal is not carried on the hydroxy apatite as was the case with this practical example. A metal element and a calcium phosphate are simply mixed as powders or the

powders are simply sintered so that the interaction of the metal element and the calcium phosphate is weaker at the atomic level and the dispersibility is low. As a result, it was found that it has poor oxidation and decomposition power due the metal element and the deodorizing power is insufficient.

[0094]

Practical Examples 50 through 64

Next, we shall explain practical examples and comparative examples using a deodorizing agent wherein four to five kinds of elements selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element are carried on a calcium phosphate group compound and at least one type of element selected from a group made up of a titanium element, silver element and manganese element is carried on the abovementioned deodorizing element.

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[0095]

We suspended 135 g of the hydroxy apatite (mol ratio of calcium element and phosphorus element: calcium element / phosphorus element = 1.67) synthesized using the

conventional solution phase method as a method for synthesizing the hydroxy apatite and made a slurry of it. In addition, we weighed out the metal element of the type and in the amount indicated in Table 1 below at a prescribed quantity in the form of a metal salt and dissolved it in 500 ml of distilled water.

[0096]

We added an aqueous solution of this slurry and the metal salt and stirred it for 24 hours at room temperature while maintaining a constant pH. Then, we washed the precipitate thoroughly in distilled water and dried it for 48 hours at 120°C. After it had dried, we pulverized it in a sieve and produced the deodorizing agent. However, it should be noted that the pH was adjusted using phosphoric acid and sodium hydroxide. We adjusted the pH to 4.0 in Practical Example 50 and to 6.0 in Practical Examples 51 through 64.

[0097]

The abovementioned metal salts used were as follows: nitrates of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as the iron salt;  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  as the copper salt;  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as the zinc salt;

Ni  $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  for the nickel salt; and Al  $(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as the aluminum salt.

[0098]

Fe, Cu, Zn, Ni and Al in Table 2 indicate the metal ions of an aqueous nitrate solution mixed with the slurry carrier. The amount of the metal salt used (g) and the amount of each of the metal ions or metal elements carried on the hydroxy apatite (HAp) carrier are indicated (value within parentheses: wt %).

[0099]

Table 2A (Amount of Metal Salt Mixed

Practical Example	Fe	Cu	Zn	Ni	Al	Ti	Mn	Ag
50	117.0g (12%)	61.0g (12%)	73.0g (12%)	20.0g (3%)	113.0g (6%)	—	—	—
51	117.0g (12%)	61.0g (12%)	73.0g (12%)	20.0g (3%)	113.0g (6%)	—	—	—
52	97.5g (10%)	50.8g (10%)	60.8g (10%)	20.0g (3%)	113.0g (6%)	—	—	—
53	97.5g (10%)	50.8g (10%)	60.8g (10%)	20.0g (3%)	56.5g (3%)	—	—	—
54	97.5g (10%)	50.8g (10%)	60.8g (10%)	6.7g (1%)	18.8g (1%)	—	—	—
55	78.0g (8%)	40.7g (8%)	48.7g (8%)	6.7g (1%)	18.8g (1%)	—	—	—
56	0.0g (0%)	101.7g (20%)	121.7g (20%)	20.0g (3%)	113.0g (6%)	—	—	—
57	0.0g (0%)	61.0g (12%)	73.0g (12%)	20.0g (3%)	113.0g (6%)	—	—	—

[0100]

Table 2B (Amount of Metal Salt Mixed)

Practical Example	Fe	Cu	Zn	Ni	Al	Ti	Mn	Ag
58	117.0g (12%)	0.0g (0%)	73.0g (12%)	20.0g (3%)	113.0g (6%)	—	—	—
59	117.0g (12%)	61.0g (12%)	0.0g (0%)	20.0g (3%)	113.0g (6%)	—	—	—
60	117.0g (12%)	61.0g (12%)	73.0g (12%)	0.0g (0%)	113.0g (6%)	—	—	—
61	117.0g (12%)	61.0g (12%)	73.0g (12%)	20.0g (3%)	0.0g (0%)	—	—	—
62	78.0g (8%)	40.7g (8%)	48.7g (8%)	6.7g (1%)	56.5g (3%)	46.6g (3%)	—	—
63	78.0g (8%)	40.7g (8%)	48.7g (8%)	6.7g (1%)	56.5g (3%)	—	18.9g (3%)	—
64	78.0g (8%)	40.7g (8%)	48.7g (8%)	6.7g (1%)	56.5g (3%)	—	—	6.4g (3%)

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[0101]

#### Deodorizing Effect Test

We measured the amount of deodorization of foul-smelling substances (odorants): ammonia ( $\text{NH}_3$ ), trimethylamine ( $(\text{CH}_3)_3\text{N}$ ), methyl mercaptan ( $\text{CH}_3\text{SH}$ ) for the deodorizing agents in Practical Examples 50 through 64 and in Comparative Example 7 (activated carbon: specific surface area  $1107 \text{ m}^2/\text{g}$ ) using the test method indicated below. In addition, the test conditions (repeated tests) are indicated in Table 3 below.

[0102]

#### 1. Ammonia Deodorizing Test

We injected 30 mL of aqueous ammonia at a concentration of 29 wt % in a 100 mL capacity vial and sealed it using an aluminum seal. We collected the ammonia gas which had been generated in the container and used it for the ammonia deodorizing test.

[0103]

We weighed out 0.5 g each of the deodorizing agent in Practical Examples 50 through 64 and Comparative Example 7, placed them respectively in a 1 L capacity tetrapak and fed air into it. Next, we injected ammonia gas into a tetrapak



containing the deodorizing agent, kept it for 30 minutes at a prescribed temperature and then measured the residue concentration using a gas detection tube.

[0104]

We repeated these operations until the measuring limit of the abovementioned gas detection tube was reached. This means that we measured the time the deodorizing effect of the deodorizing agent persisted converting to time measured the number of times the ammonia gas was sealed in until the measuring limit of the abovementioned gas detection tube was reached. However, it should be noted that the test was carried out at 0°C, 23° and 40°C. Furthermore, the concentration of the ammonia gas added per time was 2000 ppm.

[0105]

## 2. Trimethyl Amine Deodorizing Test

We injected 30 mL of trimethyl amine at a concentration of 30 wt % in a 100 mL capacity vial and sealed it with an aluminum seal. We collected the trimethyl amine gas generated inside the container using an injection syringe and used it for the trimethyl amine deodorizing test.

[0106]

We weighed out 0.5 g each of the deodorizing agent in Practical Examples 50 through 64 and Comparative Example 7, placed them respectively inside a 1 L capacity tetrapak and fed air into it. Next, we injected trimethyl amine gas into a tetrapak containing the deodorizing agent. We kept it for 30 minutes at a prescribed temperature and measured the residual concentration using a gas detection tube.

[0107]

We again injected the same amount of trimethyl amine gas into the tetrapak and kept it for 30 minutes at a prescribed temperature and then measured the residue concentration. We repeated these operations until we reached the measuring limit of the gas detection tube. In other words, we measured the deodorizing persistence time of the deodorizing agent converting to measured time the number of times the trimethyl amine gas was sealed in right before the measuring limit of the gas detection tube was reached. However, it should be noted that the test was carried out at temperatures of 0°C, 23°C and 40°C. Furthermore, the concentration of the trimethyl mercaptan gas added per time was 1000 ppm.

[0108]

### 3. Methyl Mercaptan Deodorizing Test

We used a methyl mercaptan standard solution having a 0.1 wt % concentration for the methyl mercaptan deodorizing test.

[0109]

We weighed out 0.1 g each of the deodorizing agents in Practical Example 50 through 64 and Comparative Example 7 and placed these respectively in a 1 L capacity tetrapak and fed air into it. Next, we injected methyl mercaptan gas into a tetrapak containing the deodorizing agent. We kept it for 30 minutes at a prescribed temperature and measured the residue concentration using a gas detection tube.

[0110]

We again injected the same amount of methyl mercaptan gas into a tetrapak and kept it for 15 minutes at a prescribed temperature and then measured the residue concentration. We repeated these operations until the measuring limit of the abovementioned gas detection tube was reached. In other words, we measured the deodorizing persistence time of the deodorizing agent converting to

measured time the number of times the methyl mercaptan gas was sealed in right before the measuring limit of the gas detection tube was reached. However, it should be noted that the tests were carried out at temperatures of 0°C, 23°C and 40°C. Furthermore, the concentration of the methyl mercaptan gas per time was 130 pp.

[0111]

Results (number of times deodorizing effect persisted) under the abovementioned measuring conditions are indicated in Table 4 below.

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[0112]

Table 3 (Repeated Test Measuring Conditions)

	Initial Added		Amount of
	Concentration	Interval Time	Sample
Ammonia	2,000 ppm	30 min	0.5 g
Trimethyl amine	1,000 ppm	30 min	0.5 g
Methyl mercaptan	130 ppm	15 min	0.1 g

[0113]

Table 4A (Number of Continuous Times for Deodorizing  
Effect:

( ) indicate Final Residue Concentration (ppm))

	Temperature	Ammonia	Trimethyl	Methyl
			Amine	Mercaptan
Practical Example 50	0°	6 times (500)	Twice (42)	3 times (20)
	23°	8 times (500)	Twice (42)	4 times (5)
	40°C	10 times (400)	3 times (35)	6 times (50)
Practical Example 51	0°C	4 times (400)	Once (14)	Twice (50)
	23°C	5 times (300)	Once (14)	3 times (40)
	40°C	8 times (500)	Twice (63)	4 times (50)
Practical Example 52	0°C	4 times (500)	Once (63)	Twice (60)
	23°C	4 times (200)	Once (14)	3 times (10)
	40°C	6 times (600)	Twice (70)	3 times (60)
Practical Example 53	0°C	3 times (500)	Once (63)	3 times (50)
	23°C	4 times (300)	Once (63)	4 times (60)
	40°C	5 times (600)	Twice (70)	5 times (50)
Practical Example 54	0°C	3 times (500)	Once (70)	3 times (100)
	23°C	3 times (300)	Once (63)	3 times (80)
	40°C	4 times (400)	Once (14)	4 times (50)
Practical Example 55	0°C	2 times (700)	Once (62)	Twice (70)
	23°C	3 times (400)	Once (35)	3 times (50)
	40°C	4 times (300)	Once (14)	3 times (40)

[0114]

Table 4B (Continuous Number of Times for Deodorizing

Effect:

( ) indicates Final Residue Concentration (ppm)

Practical Example 56	0°C	2 times (700)	Once (70)	Once (70)
	23°C	3 times (500)	Once (56)	Once (50)
	40°C	4 times (600)	Once (42)	Once (40)
Practical Example 57	0°C	Twice (650)	Once (56)	Once (70)
	23°C	3 times (450)	Once (56)	Once (40)
	40°C	4 times (500)	Once (42)	Once (40)
Practical Example 58	0°C	3 times (450)	Once (56)	Once (70)
	23°C	4 times (600)	Once (42)	Once (50)
	40°C	5 times (800)	Once (35)	Once (40)
Practical Example 59	0°C	3 times (500)	Once (56)	Twice (70)
	23°C	4 times (500)	Once (42)	Twice (50)
	40°C	5 times 400)	Once (35)	Twice (30)
Practical Example 60	0°C	4 times (600)	Once (14)	Twice (70)
	23°C	5 times (500)	Twice (56)	Twice (50)
	40°C	7 times (400)	Twice (35)	Twice (30)
Practical Example 61	0°C	Twice (500)	Once (56)	Once (70)
	23°C	3 times (500)	Twice (42)	Twice (50)
	40°C	4 times (400)	Twice (35)	Twice (30)

[0115]

Table 4C (Continuous Number of Times for Deodorizing

Effect:

( ) indicates Final Residue Concentration (ppm) )

Practical Example 62	0°C	2 times (500)	Once (63)	Twice (70)
	23°C	3 times (450)	Once (56)	3 times (40)
	40°C	4 times (500)	Once (42)	4 times (40)
Practical Example 63	0°C	3 times (500)	Once (63)	Twice (70)
	23°C	3 times (350)	Once (56)	3 times (50)
	40°C	5 times (800)	Twice (70)	4 times (40)
Practical Example 64	0°C	3 times (500)	Once (63)	Twice (50)
	23°C	3 times (350)	Once (35)	3 times (50)
	40°C	4 times (400)	Twice (70)	4 times (40)
Practical Example 65	0°C	Once (500)	Twice (63)	Once (50)
	23°C	Once (450)	Twice (35)	Once (40)
	40°C	0 times (>:1000)	Twice (70)	0 times (> 140)

[0116]

#### <Results>

It can be seen from the results above that the deodorizing agent in this practical example of the present invention has a powerful deodorizing effect on ammonia, trimethyl amine and methyl mercaptan, that the temperature rises and at the same time and that the deodorizing power tends to be improved as well.

[0117]

It can also be seen that the deodorizing effect of the deodorizing agent in this practical example of the present invention is equal to or greater than that of activated carbon for at least one of the abovementioned odorants. In particular, it can also be seen that the deodorizing effect of the deodorizing agent in Practical Example 50 was effective for any of the abovementioned odorants in a temperature range of 0 to 40°C and could be used longer (many times) than in Comparative Example 7.

[0118]

It can also be seen that in comparing Practical Example 50 and Practical Example 51, the pH for Practical Example 50 when the deodorizing agent in this practical example of the present invention is being manufactured is somewhat superior.

[0119]

It can also be seen from Practical Examples 56 through 61 that the effect of the deodorizing agent on ammonia, trimethyl amine, methyl mercaptan and the like is different depending on the type of carrier metal used.



[0120]

It can also be seen from Practical Examples 62 to 64 that when an iron element, copper element, zinc element, nickel element and aluminum element are all carried and at least one type of element selected from a group made up of a titanium element, silver element and manganese element is carried, a deodorizing effect equal to or greater than when these are not carried (for example, Practical Example 55) can be obtained for a variety of odorants.

[0121]

It can also be seen that an iron element, copper element, zinc element, nickel element and aluminum element should be carried and that the iron element, copper element, and zinc element should be carried in the range of 6 to 12 wt % and the nickel element and the aluminum element should be carried in the range of 1 to 6 wt %.

[0122]

We have explained the present invention based on practical examples of it and this practical example may be further modified based on the technical concept of the present invention.

[0123]

For example, besides using hydroxy appatite as a carrier, appatite fluoride, appatite chloride and other halogenated appatites may be used as well.

[0124]

In addition, besides the calcium phosphate group compounds and the various metal constituents indicated, other well-known additives may be contained as well.

[0125]

In addition, when the deodorizing agent in the present invention is used in an environment where ammonia, trimethyl amine, methyl mercaptan and other odorants are specified, when ammonia is generated in large amounts and the amount of the aluminum element in the deodorizing element is increased, the amount and type of carrier metal can be selected depending on the environment so that ammonia in particular can be deodorized efficiently.

[0126]

[Actions and Effect of Invention]

The deodorizing agent in the present invention is such that at least one type of element selected from a group

made up of an iron element, copper element, zinc element, nickel element and aluminum element is carried on a carrier made up of a calcium phosphate group calcium so that ammonia, trimethyl amine, methyl mercaptan and other foul-smelling substances (odorants) can be adsorbed efficiently. These foul-smelling substances (odorants) can be removed by oxidation efficiently through the catalytic effect.

[0127]

In addition, the production method in the present invention involves adding at least one type of element selected from a group made up of an iron element, copper element, zinc element, nickel element and aluminum element to slurry of a calcium phosphate group compound and allowing it to dry. Each of the abovementioned elements may be carried sufficiently by ion replacement and / or adsorption on the calcium phosphate group compound.

[Brief Explanation of Figures]

[Figure 1] A graph indicating changes in the amount of ammonia adsorbed by the total amount of metal carried and indicating as well the deodorizing effect of the deodorizing agent in the present invention on ammonia.

[Figure 2] A graph indicating changes in the amount of methyl mercaptan adsorbed by the total amount of metal carried and indicating as well the deodorizing effect of the deodorizing agent in the present invention on methyl mercaptan.

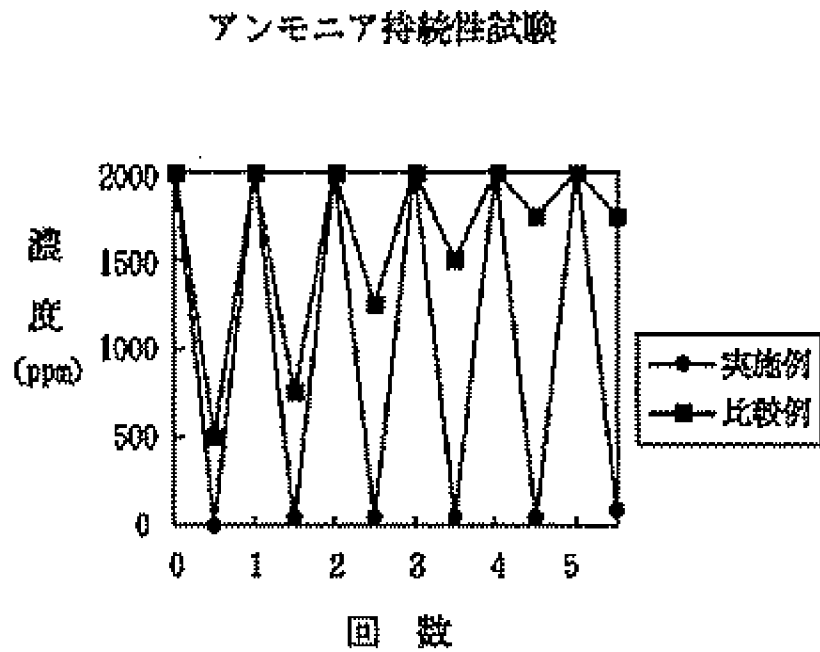
[Figure 3] A graph indicating changes in the amount of ammonia adsorbed by the total amount of metal carried and indicating as well the deodorizing effect of the deodorizing agent in the present invention on ammonia.

[Figure 4] A graph indicating changes in the amount of methyl mercaptan adsorbed by the amount of one type of metal carried and indicating as well the deodorizing effect of the deodorizing agent in the present invention on methyl mercaptan.

[Figure 5] A graph indicating the persistence of the deodorizing effect on the ammonia in the practical examples and the comparative examples.

[Figure 6] A graph indicating the persistence of the deodorizing effect on the methyl mercaptan.

[Figure 5]



[Captions:

Above graph: Ammonia Persistence Test

Left margin: concentration (ppm)

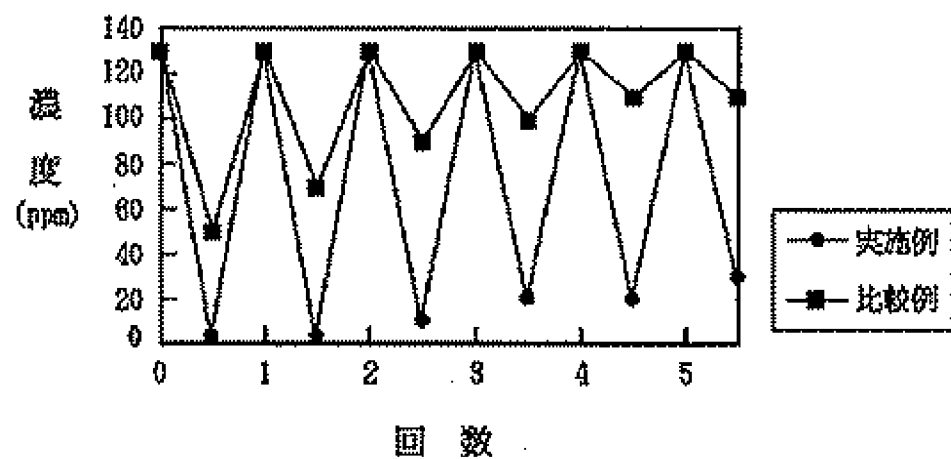
Right margin: Practical Example

Comparative Example

Beneath figure: Number of Times]

[Figure 6]

# メチルメルカプタン持続性試験



[Captions:

Above graph: Methyl Mercaptan Persistence Test

Left margin: Concentration (ppm)

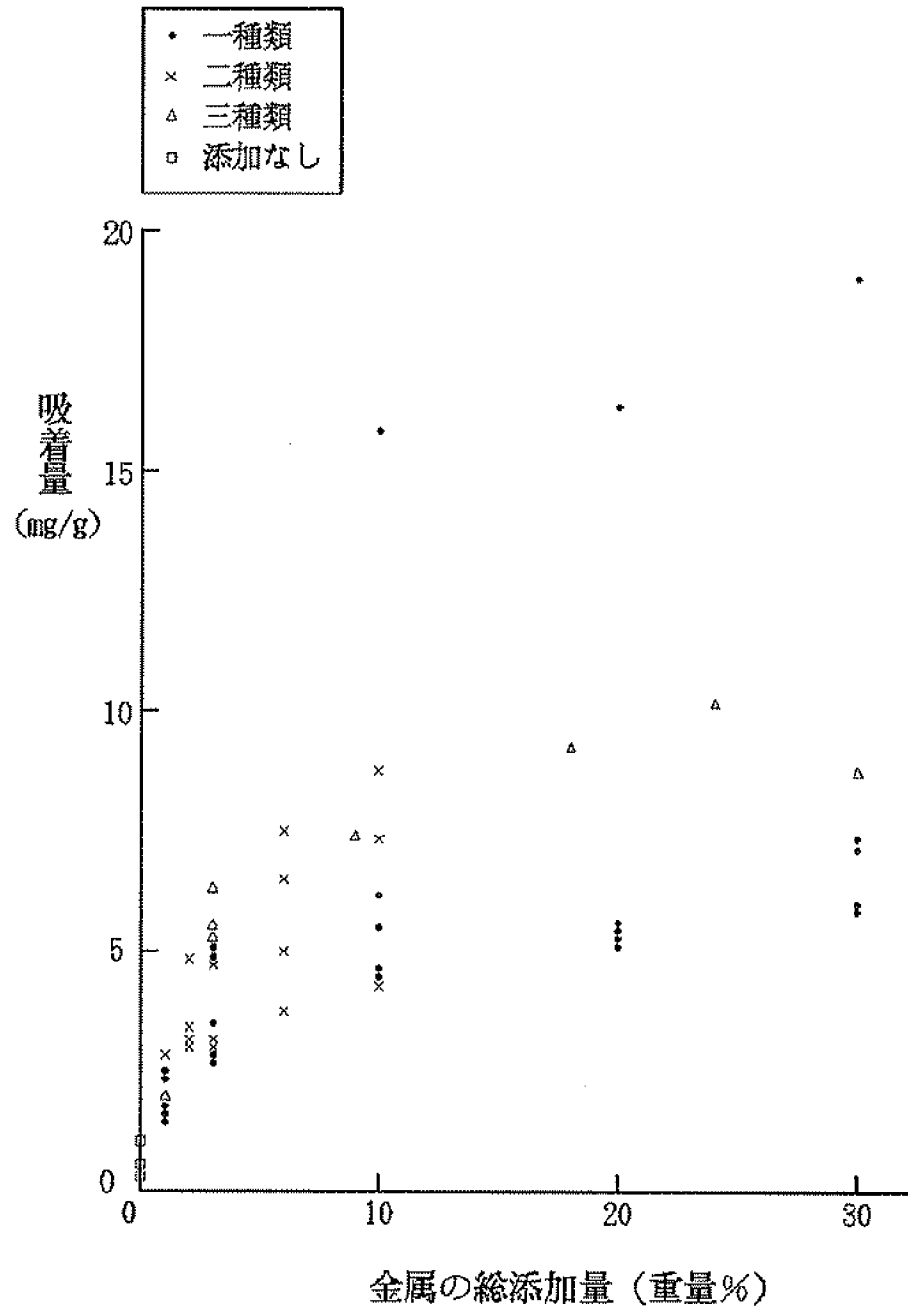
Right margin: Practical Example

Comparative Example

Beneath graph: Number of Times]

[Figure 1]

### アンモニア (NH<sub>3</sub>)に対する消臭効果



[Captions:

Above graph: Deodorizing Effect on Ammonia (NH<sub>3</sub>)

Left margin: Amount of Adsorption (m/g)

Upper left:

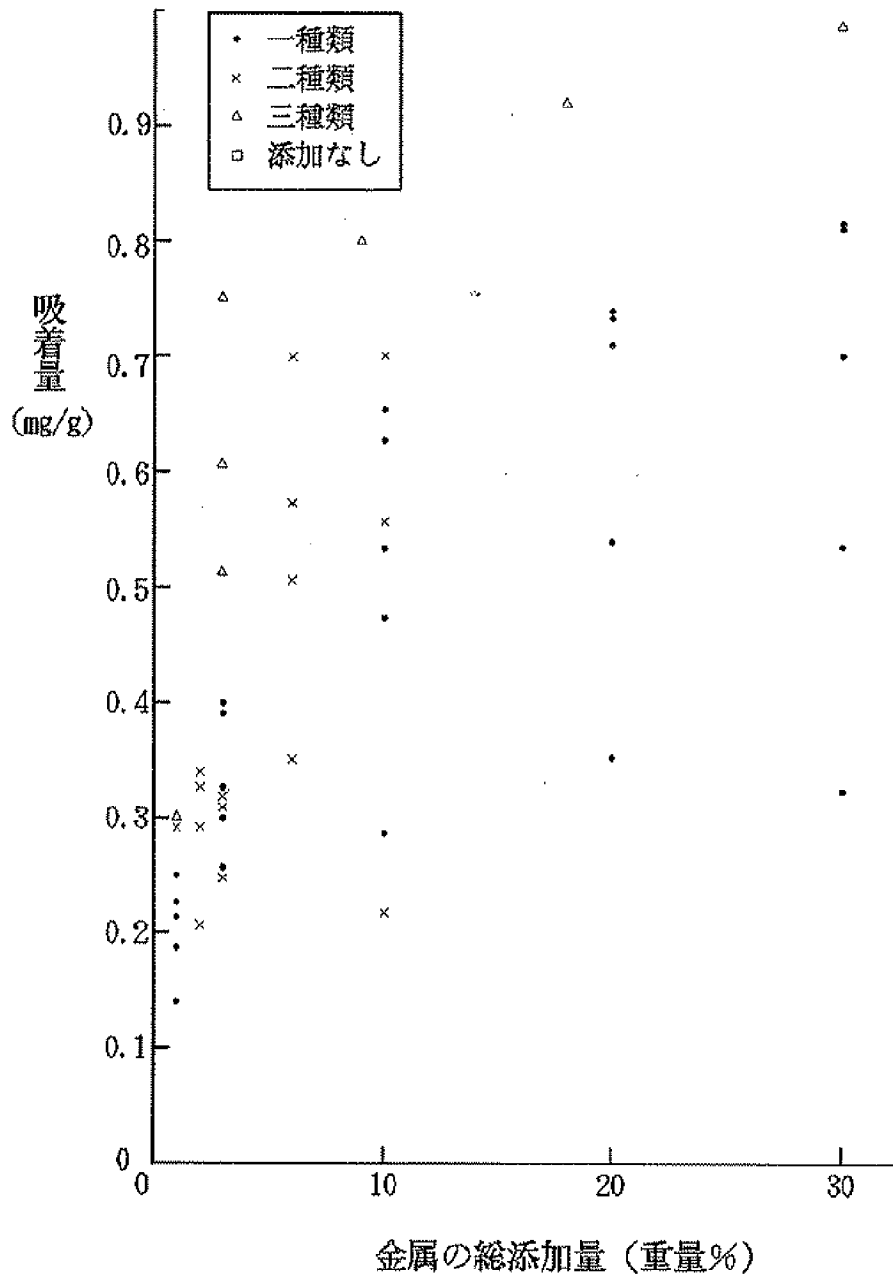
- One type
- X Two types
- $\Delta$  Three types
- X None added

Beneath graph: Total Amount of Metal Added (wt %)

[Figure 2]



メチルメルカプタン ( $\text{CH}_3\text{SH}$ ) に対する消臭効果



[Captions:

Above graph: Deodorizing Effect on Methyl Mercaptan ( $\text{CH}_3\text{SH}$ )

[Captions:

Above graph: Deodorizing Effect on Ammonia ( $\text{NH}_3$ )

Left margin: Amount of Adsorption (m/g)

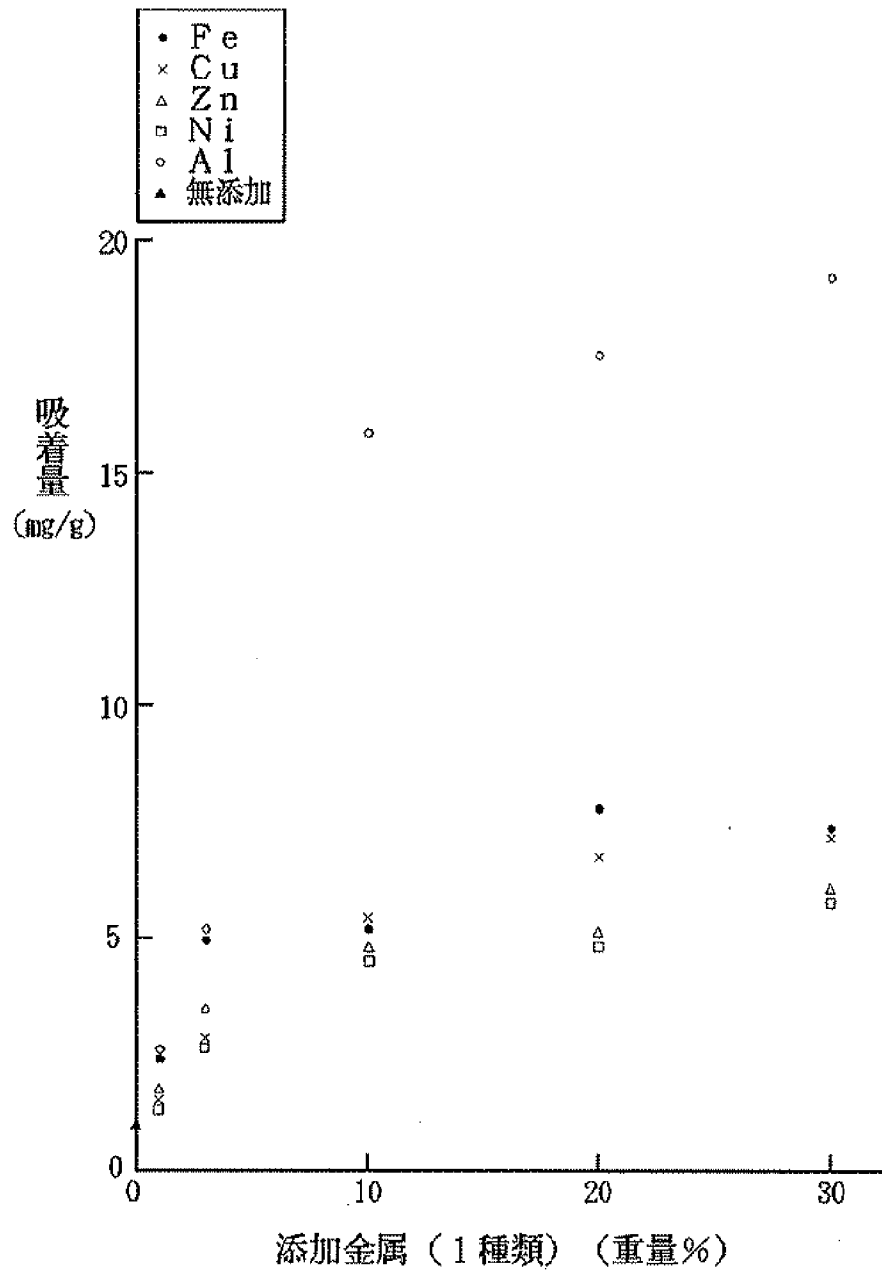
Upper left:

- One type
- X Two types
- $\Delta$  Three types
- X None added

Beneath graph: Total Amount of Metal Added (wt %)]

[Figure 3]

アンモニア (NH<sub>3</sub>)に対する消臭効果



[Captions:

Above graph: Deodorizing Effect on Ammonia (NH<sub>3</sub>)

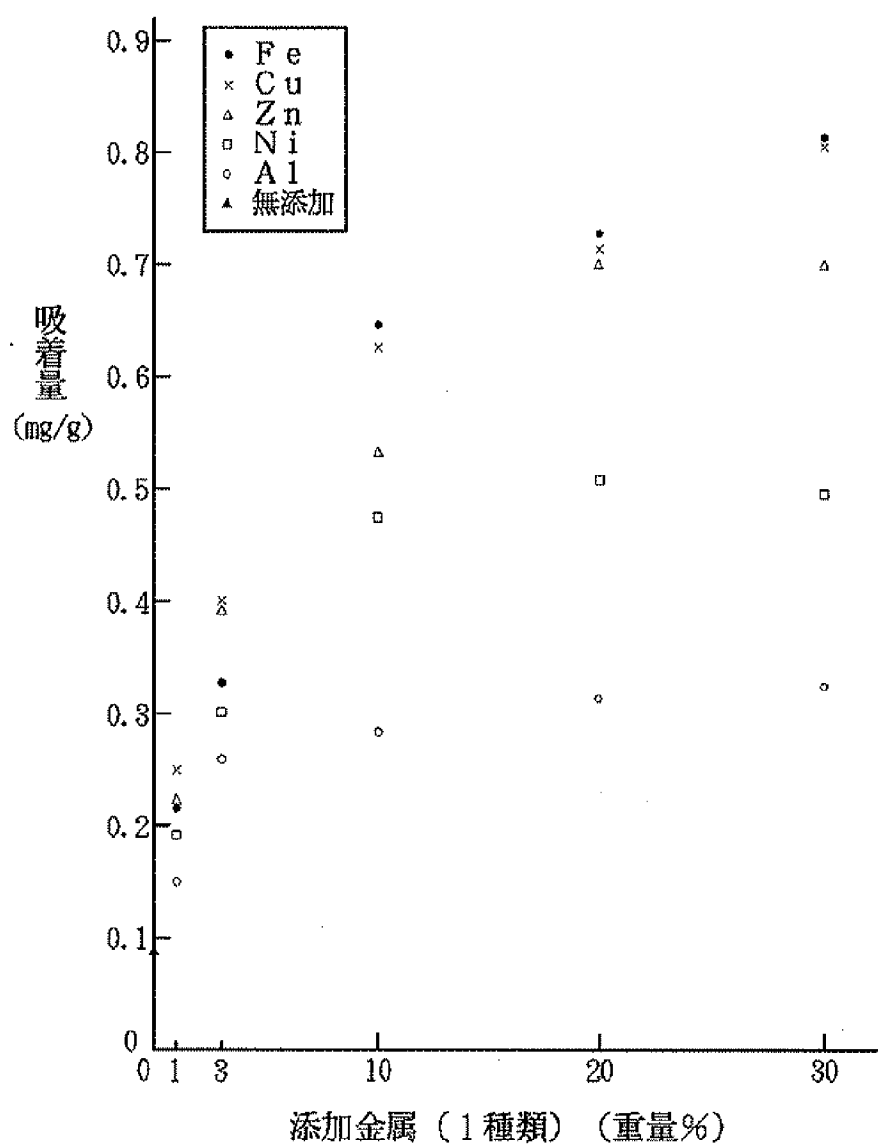
Left margin: Amount adsorbed (mg/g)

Upper left:  $\Delta$  none added

Beneath graph: Metal Added (one type) (wt %)

[Figure 4]

メチルメルカプタン ( $\text{CH}_3\text{SH}$ ) に対する消臭効果



[Captions:

Above graph: Deodorizing Effect on Methyl Mercaptan

(Ammonia ( $\text{NH}_3$ ))

Left margin: Amount adsorbed (mg/g)

Upper left:  $\Delta$  none added

Beneath graph: Metal Added (one type) (wt %)]